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Protocol for Assessment of Human Exposure to Airborne Pesticides. User's Guide

(U.S.) Health Effects Research Lab.
Research Triangle Park, NC

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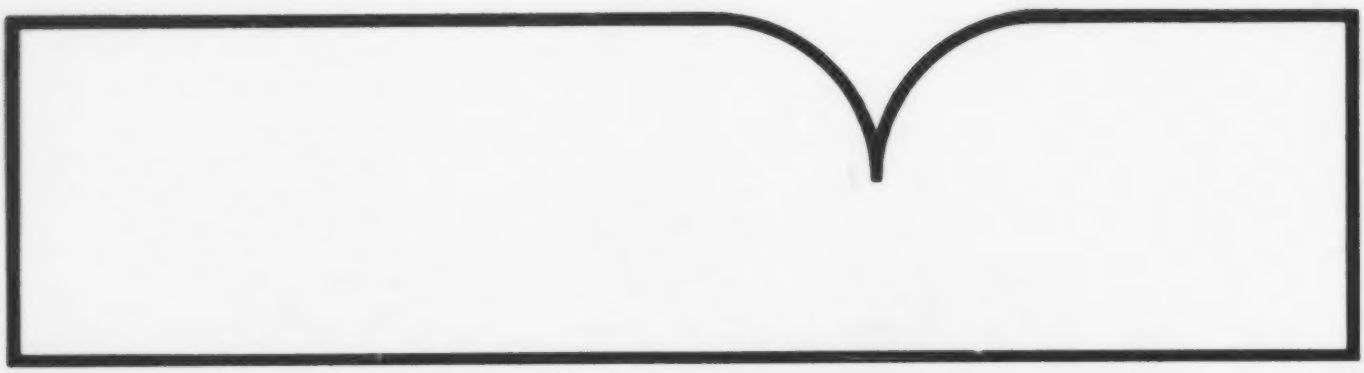

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August 1980

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EPA

Users Guide

Protocol for Assessment of Human Exposure to Airborne Pesticides

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Descriptions are given of pumps, sorbents, calibration methods, and preparations necessary for accurate data collections. The determination of sampling efficiencies and respiratory exposure is also discussed.

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PROTOCOL FOR ASSESSMENT OF HUMAN EXPOSURE TO AIRBORNE PESTICIDES

by

Robert G. Lewis, Merrill D. Jackson and Kathryn E. MacLeod

Environmental Toxicology Division
Health Effects Research Laboratory
Research Triangle Park, North Carolina 27711

HEALTH EFFECT RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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FOREWORD

The many benefits of our modern, developing, industrial society are accompanied by certain hazards. Careful assessment of the relative risk of existing and new man-made environmental hazards is necessary for the establishment of sound regulatory policy. These regulations serve to enhance the quality of our environment in order to promote the public health and welfare and the productive capacity of our Nation's population.

The Health Effects Research Laboratory, Research Triangle Park, conducts a coordinated environmental health research program in toxicology, epidemiology, and clinical studies using human volunteer subjects. These studies address problems in air pollution, non-ionizing radiation, environmental carcinogenesis and the toxicology of pesticides as well as other chemical pollutants. The Laboratory participates in the development and revision of air quality criteria documents on pollutants for which national ambient air quality standards exist or are proposed, provides the data for registration of new pesticides or proposed suspension of those already in use, conducts research on hazardous and toxic materials, and is primarily responsible for providing the health basis for non-ionizing radiation standards. Direct support to the regulatory function of the Agency is provided in the form of expert testimony and preparation of affidavits as well as expert advice to the Administrator to assure the adequacy of health care and surveillance of persons having suffered imminent and substantial endangerment of their health.

One mission of the Environmental Protection Agency is to monitor the air for pesticides. Pursuant to this mission, this project was

undertaken by HERL to establish uniform methodology for obtaining adequate data on the contamination of the atmosphere by pesticides. This will give EPA the ability to define the threat of atmospheric pesticidal pollutants and lead to the determination of their effect on the general population and the ecosystem.

F. G. Hueter, Ph.D.
Director
Health Effects Research Laboratory

ABSTRACT

The Environmental Protection Agency has been given the authority for monitoring the air for pesticides. This protocol reports on methodology that has been developed to assure that the air samples collected will give adequate information on the exposure of the general population to pesticidal air pollutants.

Descriptions are given of pumps, sorbents, calibration methods, and preparations necessary for accurate data collections. The determination of sampling efficiencies and respiratory exposure is also discussed.

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I. INTRODUCTION

Pesticides in air represent an important class of toxic pollutants, which may have chronic deleterious effects on human health and ecological balance. In 1963, the President's Science Advisory Committee recommended that the air be continuously monitored for pesticides. The authority for such monitoring in the U.S. has been granted to the Environmental Protection Agency under the Clean Air Act as amended in December 1970, and the Federal Insecticide, Fungicide, and Rodenticide Act as amended in 1972.

Presently, there are only limited data concerning the contamination of the atmosphere by pesticides, especially in urban areas. Information relating to transport or ambient trends is even less available. Such information must be obtained before total air quality can be defined and before the threat of atmospheric pesticidal pollutants to the general populace and the ecosystem can be determined.

The determination of pesticides in the ambient air is a formidable task.[1] There are hundreds of pesticides registered for use in the U.S., many of which are potential air pollutants. These pesticides may exist in air as vapors, aerosols, or adsorbed on suspended particulate matter; thus, their collection is complicated. Pesticides are usually present in air at levels far lower than those found in crop residues for which most methods of analysis are designed;

hence, their detection is difficult. Metabolites and degradation products of pesticides, which are sometimes considerably more toxic than the parent pesticide, are, of course, at even lower atmospheric concentrations.

Most of the existing data concerning the nature and degree of contamination of the ambient atmosphere by pesticides was collected over the period from 1970 to 1972 by the EPA. The sampling method utilized was based on impingement in ethylene glycol, which was expensive and cumbersome to use and did not provide an adequate sample size to permit subnanogram per cubic meter detectabilities for most pesticides. During the past several years, EPA has developed a high volume air sampler that is believed to better serve the needs for pesticide ambient air monitoring. This sampling device and others for indoor air sampling, crop re-entry monitoring, and work-place and personnel monitoring are described.

II. AMBIENT AIR SAMPLING:

1. Descriptions of Ambient Air Samplers

For ambient (uncontaminated) air, sufficiently large samples must be taken to permit detection and measurement at ultra-trace levels (pg/m^3 to ng/m^3). Such sampling should be performed over an entire diurnal cycle if results are to be

representative of the average quantities of the substances normally present in the atmosphere.

a. The sampler developed by EPA[2,3,4] has been referred to as the EPA/SURC sampler (Fig. 1), since it is similar to a high volume pesticide air sampler designed for EPA by Syracuse University Research Corporation.[5] The device uses a Hi-Vol pump and shelter, and draws air through a glass fiber filter (to collect particulate matter) and a solid sorbent cartridge (to trap vapors) at sampling rates up to 280 liters/minute. The sampler can be used with a wide variety of sorbents in a manner that permits their continual re-use. It is designed for low cost and simple operation. The sampler has been demonstrated to efficiently collect a number of organochlorine and organophosphate pesticides, and it is presently being evaluated for carbamates.

   A standard aluminum Hi-Vol sampler housing is modified by replacing the sheet aluminum support plate with one that is 9 mm thick. A second support plate is added approximately 25 cm from the bottom of the sampler to lend strength. The top plate forms the support for the blower unit and pesticide collection module as well as the necessary plumbing.

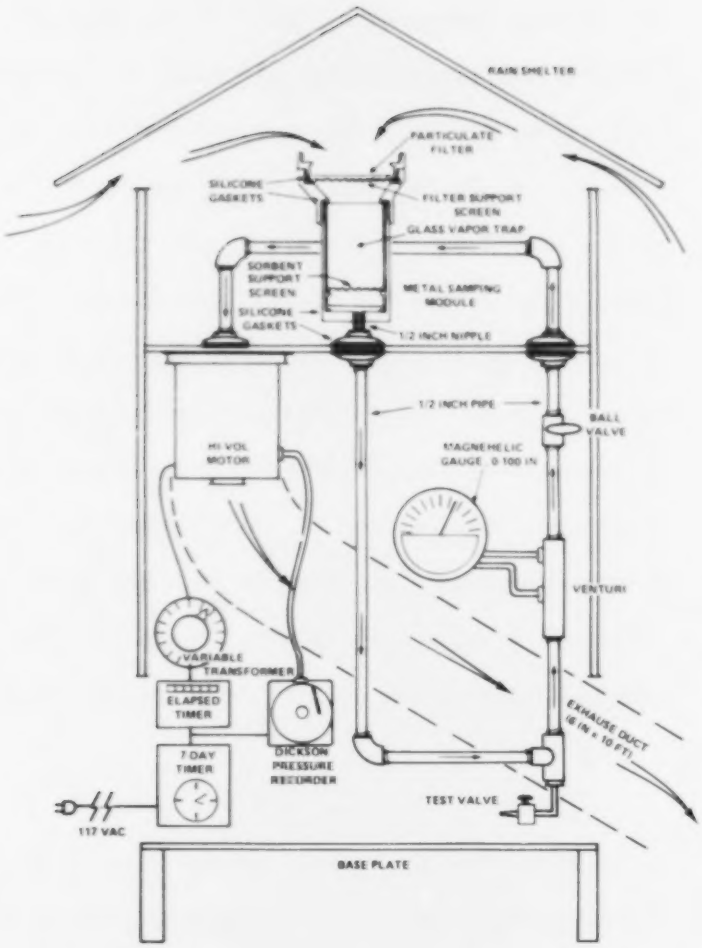

Figure 1. EPA/SURC high volume ambient air sampler for pesticides, PCBs and other organic compounds.

All parts and how they are connected are shown in Figure 1. A variable power transformer is provided to adjust the vacuum pulled by changing the motor speed. This prolongs the life of the motor. The flow is measured by two devices: a Dickson recorder (The Dickson Company, Minicorder, Design 1), which keeps a continuous record of the flow versus time, and a venturi (Barco Model BR-12402-08-31) - Magnehelic gauge (Dwyer Instruments Model 2100), used to set the flow rate of the sampler when in operation. The exhaust duct is required to stop recycling of the air.

b. PCBs (polychlorinated biphenyls) have been collected on polyurethane foam by sampling 3.4-200 m^3 of air with Bendix Hurricane dual speed pumps (National Environmental Instruments, Inc., Warwick, RI 02888, Cat. No. 16003) at flow rates of 0.1-0.5 m^3/minute.

2. Descriptions of the Sampling Modules

a. The SURC sampling module is shown assembled (a) and exploded (b) in Figure 2. The basic module consists of a 4-inch (i.d.) by 2-inch (i.d.) (10 cm x 5 cm) glass process pipe reducer (Kimax 6650, size 4, or equivalent - Part 1 in Fig. 2). This part is approximately 18 cm long. Standard glass pipe fittings (parts 2 and 3) are

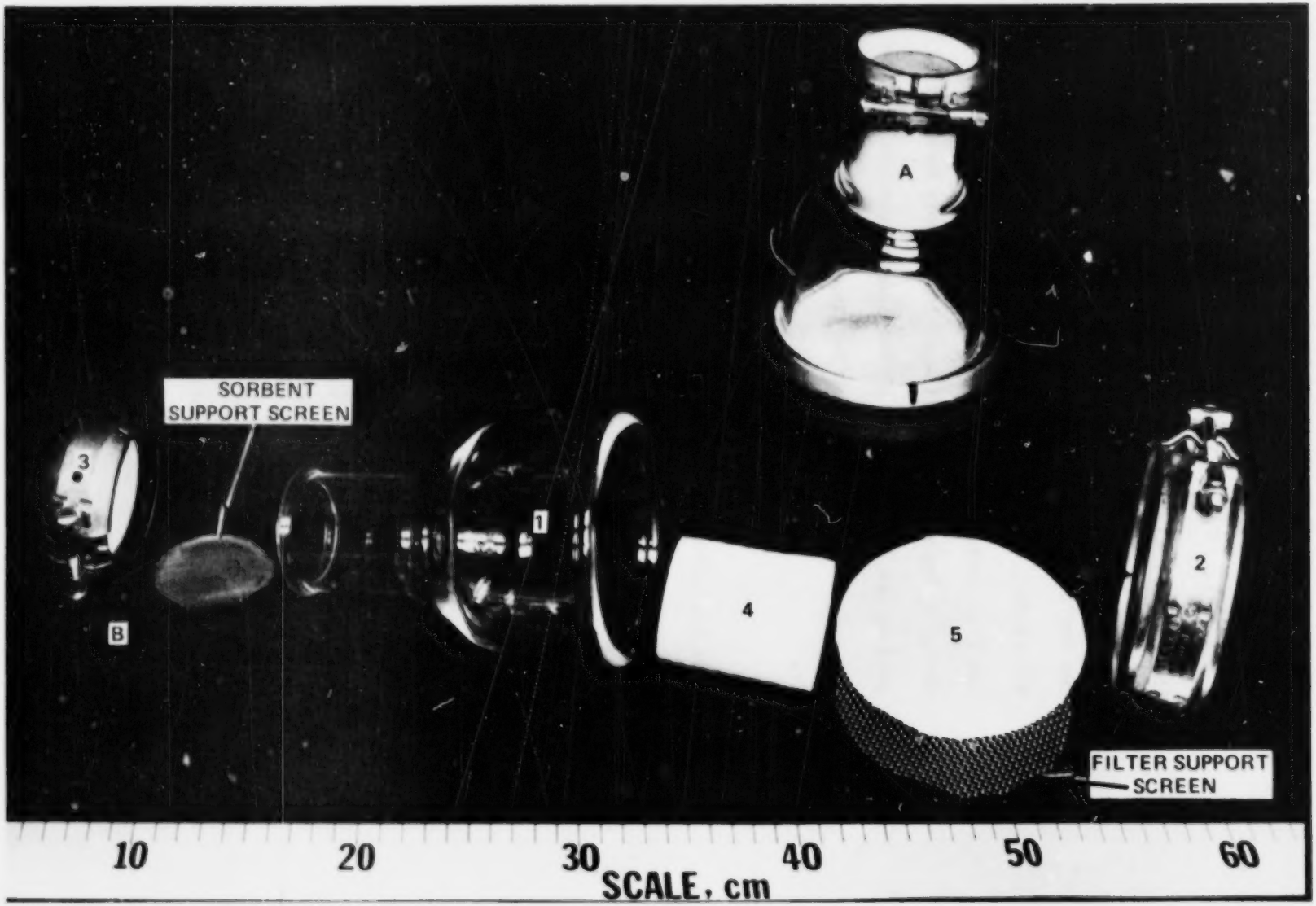

Figure 2. The SURC sampling module, assembled (a) and disassembled (b). Part 1 is a 4-in x 2-in glass process pipe reducer. Parts 2 and 3 are stainless steel pipe fittings with Teflon inserts. Part 4 is a 5.5-cm x 7.6-cm polyurethane foam cylinder and Part 5 is a Gelman Type A glass fiber filter (it is installed under Part 2).

used on each end (2-inch and 4-inch connectors). At the smaller end, a stainless steel screen (10 openings/cm) is cut to fit and installed to hold the polyurethane foam plug (4) or other sorbent in place. A piece of stainless steel screen (4 openings/cm) is cut and installed at the larger end. This holds either the glass fiber filter (5) in normal operation or wool felt filter for controlled introduction of vapors of the test compounds. When foam is used as the sorbent, the larger opening screen may be used on both ends. The lower pipe fitting (part 3) is tightened down on a 2 inch stainless steel flange.

b. EPA - SWRI Sampling System - The sampling system was developed by Southwest Research Institute[6] and was substantially modified and improved by EPA to allow use of a variety of sorbent types (Fig. 3). This module is shown in place on the sampler in Figure 1. The same sampler described under Item 1 above is used. There are two parts to the sampling system: the sampling module or cartridge and the air-tight cartridge holder.

Sampling cartridge - Borosilicate glass tubing (65 mm, OD) is cut to 125 mm in length. An indentation is formed 20 mm from one end (bottom) to provide a rim to retain a 25 mesh or larger stainless steel screen to hold the

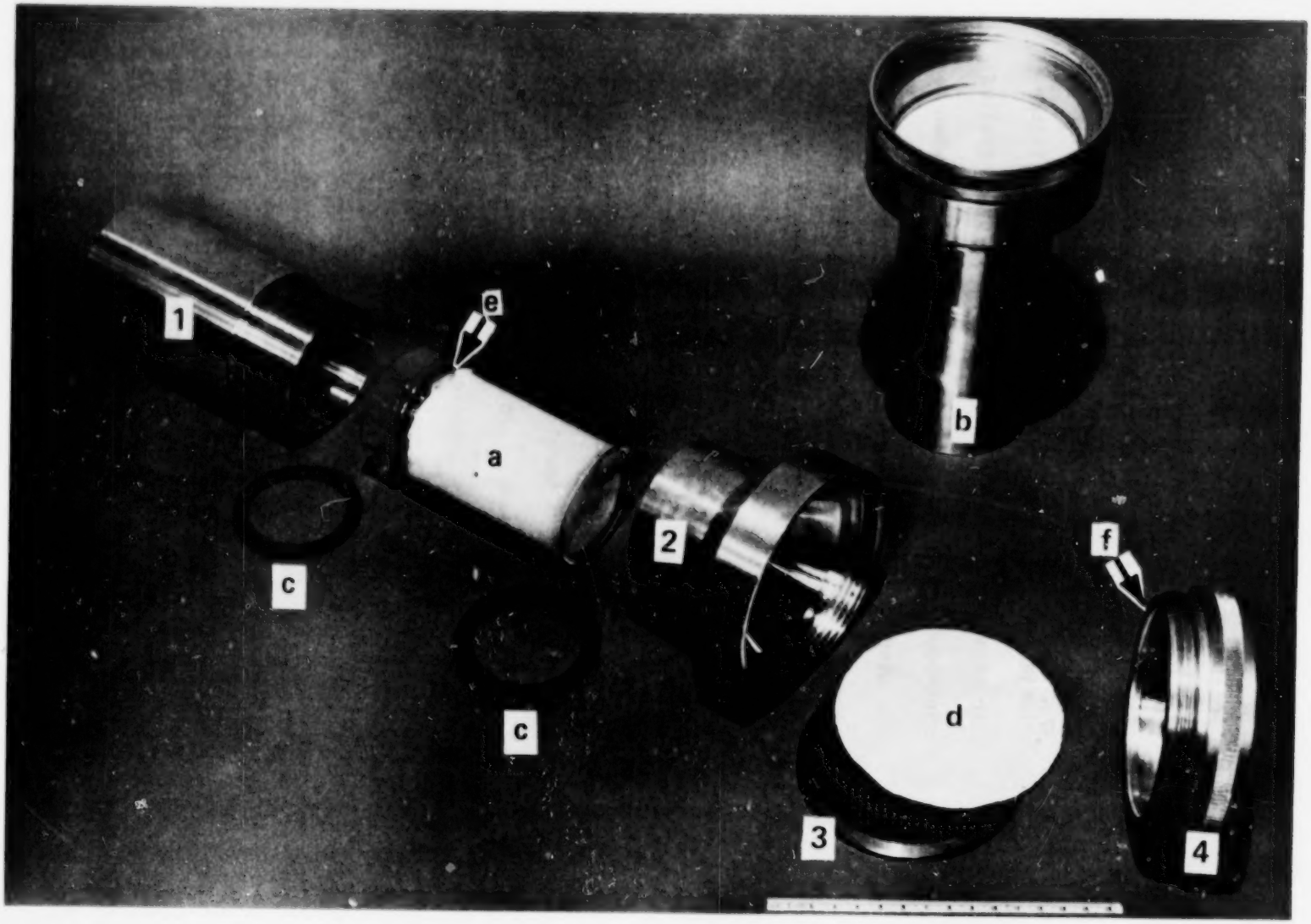

Figure 3. EPA/SWRI high-volume sampling module. (a) Sampling cartridge; (b) assembled module containing cartridge and prefilter; (c) silicone rubber gaskets; (d) glass fiber prefilter; (e) support screen; (f) silicone rubber "O"-ring. Part 1 - Cartridge receptacle. Part 2 - Prefilter adapter. Part 3 -Filter support screen. Part 4 - Filter retaining ring.

sorbent. The cartridge can then hold a polyurethane foam plug, porous (macroreticular) beads or other solid sorbents, or liquid coated beads.

This entire cartridge can be placed in a Soxhlet extractor for removal of substances collected in air. Vacuum drying at 30°C to 40°C restores the sorbent for reuse within several hours. The cartridge is shown in Figure 3 (Part a).

Cartridge holder - The basic cartridge holder is shown both assembled (b) and disassembled in Figure 3. Part 2 screws down on to Part 1 and silicone rubber (GC septum sheet stock, Supelco Catalog No. 2-04626) gaskets (c) on both ends form an air-tight seal. Part 3, a 10-mesh stainless steel screen, holds either the glass fiber filter (d) or the felt pad. Part 4 holds the filter or pad in place. Part 1 is tapped and threaded on the bottom to attach to the 1/2 inch NPT inlet of the high-volume air pumping system shown in Figure 1.

c. Bendix Hurricane Pump filter holder - The standard 10 cm filter holder is modified by attaching a cylindrical chamber, 25 cm long x 5 cm i.d., behind the filter holder with epoxy cement. Place two foam plugs, 5.5 cm diameter x 8 cm thick, in the chamber and a 10 cm diameter glass

fiber filter in front of them in the filter holder. Connect the sampler to the Bendix pump by a 7.6 meter length of Flexaust® CWC hose.

3. Calibration of Air Sampler

Refer to Figure 1 for a schematic diagram of the sampler. The needle valve is for test purposes only and is not used in normal operation. The red tap of the venturi goes to the high pressure side, and the green tap goes to the low pressure side of the Magnehelic gauge. A gasket goes between each floor flange and the base, and between the Hi-Vol housing and the base. Check these for leaks before starting. Make the modification to the motor housing shown in Figure 4.

Calibration procedure:

a. Attach the calibration venturi in place of the sampling module and tighten securely.

b. Connect a 4"-0-4" slack tube Hg manometer to the taps of the calibrated venturi. Make sure the manometer is zeroed and level. Mark this manometer to indicate that it is to be used only with the audit venturi.

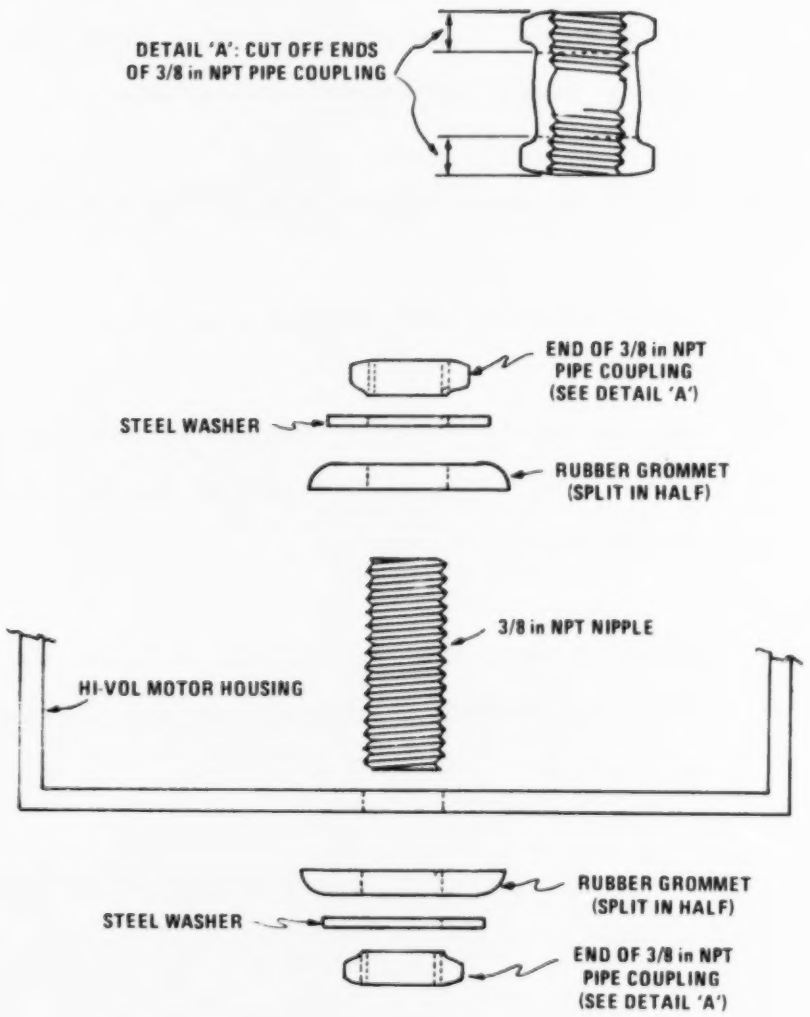

Figure 4. Device for calibration of air sampler.

c. Zero the Dickson recorder (tap the face) and the Magnehelic gauge.

d. Turn the power transformer to 100 volts and turn the switch to ON. Allow the Hi-Vol motor to warm up for several minutes before readings are taken.

e. Record the ambient temperature in °C on the data form.

f. Record the barometric pressure in mm Hg.

g. Open the ball valve fully (the pointer on either zero mark). Record the audit venturi DP, the Dickson reading, and the Magnehelic reading.

h. Close the indicator valve slightly until the Magnehelic drops approximately 5 inches (13 cm) and record a new set of readings.

i. Repeat step (h) until five spaced sets of readings are obtained.

j. Remove the calibrated venturi.

k. Prepare a calibration chart of flow rate versus meter readings as shown in Figure 5.

To calibrate Bendix high volume pumps, force the exhaust air through a restricting orifice (supplied with the pump) and measure the resulting back pressure by a gauge placed directly ahead of the orifice. A gauge calibrated by the manufacturer to read directly in ft^3/minute air flow is available.

4. Descriptions of Sampling Media (Sorbents)

Two types of sampling media are recommended for use with the EPA/SURC sampler: polyurethane foams and granular solid sorbents. Foams may be used separately or in combination with granular solids in either sampling module described previously. With the EPA/SURC module, the sorbent may be extracted and reused (after drying) without unloading the cartridge.

Polyurethane foam (PUF) - Use polyether-type polyurethane foam [density No. 3014 (0.0225 grams/cm^3), or equivalent]. This is the type of foam generally used for furniture upholstery, pillows, and mattresses. It is white and yellows on exposure to light. Use 7.6 cm (3 in.) sheet stock and cut from it cylindrical plugs that fit under slight compression in the glass cartridge or module, supported by the wire screen. For

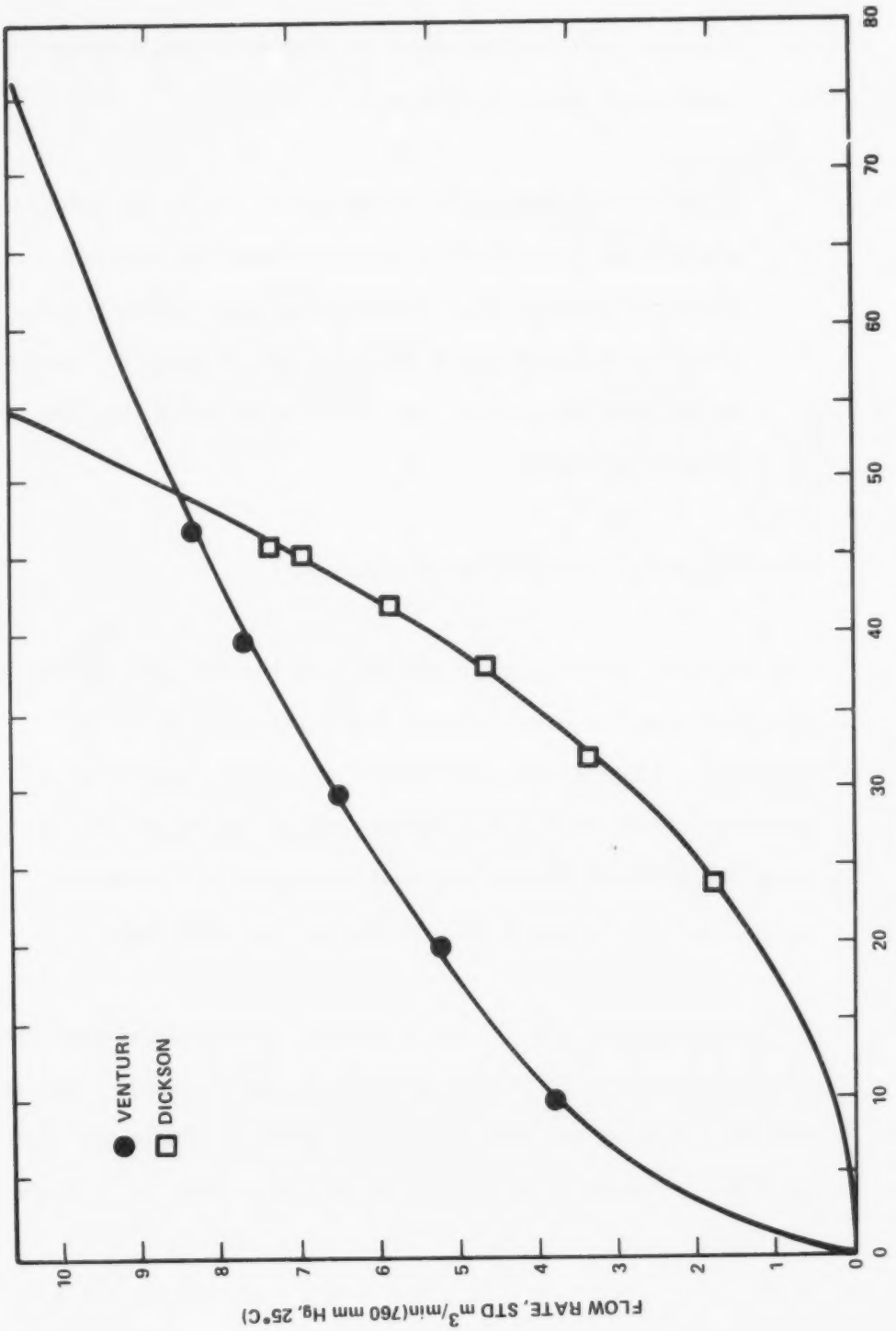

Figure 5. Calibration plot for EPA/SURC sampler.

the SURC module, the plugs should be 5.5 cm in diameter and fitted into the lower 5 cm (i.d.) chamber of the module. For the EPA/SWRI cartridge, the plug diameter should be 6.0 cm.

Granular solids - Porous (macroreticular) chromatography sorbents are recommended. Examples are Chromosorb® 102, 20- to 40-mesh (Johns-Manville, Denver, CO); Porapak® R, 50- to 80-mesh (Waters Associates, Milford, MA); Amberlite® XAD-2, 16- to 50-mesh (Rohm and Haas Co., Philadelphia, PA); Tenax®-GC, 60- to 80-mesh (Enka N.V., The Netherlands); and Florisil® PR-grade, 16- to 30-mesh (Floridin, Pittsburgh, PA). Pore sizes and mesh sizes must be selected to permit air flow rates of at least 200 liters/minute. Approximately 25 cm^3 of the sorbent is recommended. The granular solids may be "sandwiched" between two layers of polyurethane foam (a 60 mm diameter x 50 mm foam plug on top and a 60 mm diameter x 25 mm PUF plug on the botton) to prevent loss during sampling and extraction (Figure 6).

5. Preparation of Sampling Media

   a. Prepare sorbent for initial cleanup before use. For foam, cut an appropriate size cylindrical plug with a cutting tool and place in a Soxhlet extractor. For granular or porous polymeric solids, add to pre-extracted Soxhlet thimble and place in the extractor.

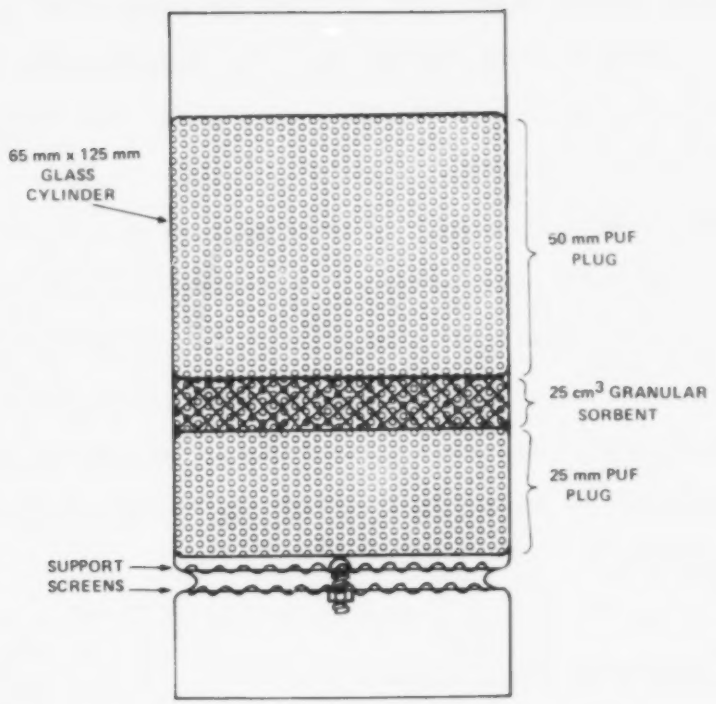

Figure 6. Dual sorbent vapor trap.

b. Extract with 5% diethyl ether in n-hexane (glass distilled, pesticide quality or equivalent) or other appropriate solvent(s) for 14-24 hours at ca 4 cycles/hour.

NOTE: To determine the blank value of each plug, extract twice for periods of 7-12 hours; concentrate the second solvent, pass through an alumina column, and analyze by GC.

c. Dry the sorbent under vacuum at 75°C.

d. Place the sorbent into glass sampling modules. For loose solids, the appropriate volume (e.g., 25 ml) should be measured and the corresponding weight recorded.

e. Place the sampling module in a sealed container or wrap in hexane-rinsed aluminum foil until ready for use.

6. Determination of Sampling Efficiencies for Specific Pesticides

a. Pesticide Retention Efficiency

No air sampler may be used for assessing of atmospheric concentrations of any compound without first determining the efficiency of the sampler to trap and retain the

compound. Determine retention efficiencies by multiple injections of microliter volumes of the pesticide of interest in n-hexane directly into the sorbent trap. After a one hour drying period, place the fortified trap in front of a second trap in the sampling system. Pump ambient air through the train for the length of time and volume to be used in the sampling (i.e., for the high volume system, 24 hours at 200-250 liters/minute) to determine breakthrough to the second trap. Exclude airborne particulate matter by means of a glass fiber prefilter.

b. Pesticide Collection Efficiency

Determine collection efficiencies by vaporizing individual compounds or mixtures into the intake of the air sampler under study. Replace the glass fiber prefilter with a pre-extracted wool felt filter (weight 14.9 mg/cm^2, thickness 0.6 mm), which is then fortified with the pesticide of interest before pulling ambient air through it and, subsequently, the vapor trap(s). Add dropwise hexane solutions containing microgram amounts of the test compounds to the filter in amounts of 1 ml or less, and evaporate the solvent before the filter is attached to the sampling module. After 24 hours of air flow, analyze

the filter and sorbent trap(s) individually. Make at least one blank determination with unfortified filters simultaneously to correct for airborne interferences and possible contamination or losses from the analytical methodology.

Perform these tests outdoors with unaltered ambient air (in a rural, nonindustrialized area) whenever possible. When required, filter the intake air through a PUF trap to remove interfering contaminants.

All pesticidal compounds used for establishing sampling efficiency should be of the highest purities obtainable. Purities should be checked before use. All solvents should be pesticide quality or equivalent.

Conduct at least six independent trials for each test compound in order to provide statistical data. Acceptable standard deviation values will depend on the nature of the pesticide. For example, for the less volatile, more chemically stable and more easily analyzed pesticides, higher precision and accuracy of results will be expected.

A sampling efficiency of 75% should, in general, be considered satisfactory for a collection medium. For the more easily trapped pesticides such as DDT and mirex, sampling efficiencies should be essentially quantitative. Reuseability of sorbents is considered important; as a guideline, at least six months of repeated use should be expected before loss in sampling efficiency is noted. The sorbents selected are also expected to vary little in trapping and retaining test compounds with changes in temperature and humidity.

7. Collection of Air Samples

A EPA/SURC air sampler may be operated at ground level or on roof tops. In urban or congested areas, it is recommended that the sampler be placed on the roof of a single-story building. The sampler should be located in an unobstructed area, at least two meters from an obstacle to air flow. The exhaust hose should be stretched out in the downwind direction, if possible. The sampler should be operated for 24 hours in order to obtain average daily levels of airborne pesticides. (Air concentration may fluctuate with time of day, temperature, humidity, wind direction and velocity, and other climatological conditions.) On and off times and weather conditions during the sampling period should be recorded. Air flow readings

should be taken (from the Magnehelic gauge) at the beginning and end of each sampling period. The chart from the Dickson recorder should be examined to note the occurrence and duration of any power failure and any change in sampling rate during the period. Blower motor brushes should be inspected frequently and replaced, as necessary. An electrical power source of 110 VAC, 15A is required.

The glass sampling cartridge and glass fiber filter (on the EPA/SWRI) should be removed from the sampler with forceps and clean, gloved hands and immediately placed in a sealed container(s) for transport to the laboratory. Similar care should be taken to prevent contamination of the filter and vapor trap when loading the sampler.

8. Results and Discussion

The greatest value of the high volume collection system is that is provides a large sampling of air (at least 300 m^3/24 hours). Thus, even with poorly trapped compounds, sufficient quantities can be collected to detect very low air concentration. For efficiently collected compounds, detection limits can be extended to the subpicogram-per-cubic-meter range, and sufficient quantities can often be trapped in 24 hours to provide for mass spectrometric confirmation.

III. SOURCE SAMPLING:

Contaminated, or source-related, atmospheres generally present less problems with respect to either the sampling process or analytical measurement because of the higher levels of pesticide present. However, source sampling often requires special sampling equipment that is portable, battery-powered, or is otherwise commensurate with specific sampling needs. Often it is also not practical (or desirable) to collect 24-hour samples. Thus a relatively high-flow device, which may also need to be portable and/or battery operated, may be required.

Monitoring atmospheres inside domiciles or workplaces requires a sampler that is unobtrusive and operates quietly, does not get in residents' or workers' way, and places little or no time or financial demands on the site owner to maintain.[7,8] Similar requirements are made on devices used to monitor inspired air. They need to be worn on the person; hence, must be battery-operated, light weight, comfortable and quiet. Ideally, they should sample air at flow rates similar to normal human respiration. Since indoor levels are generally much higher than outdoor levels, due mainly to pest control measures exercised inside domiciles and places of employment, small, low volume air samplers may be used. Sampling rates in the 1 to 10 liters/minute range are adequate and can be provided with any of several personal air sampling pumps on the market. These pumps can be operated on batteries for up to 8 hours or for longer periods if attached via a charging unit to 110 VAC house current.

1. High Volume Source Sampler

A high volume sampler developed for the U.S. Army and manufactured by Environmental Research Corporation (ERCO),[9] a subsidiary of Dart Industries, St. Paul, MN, is shown in Figure 7. Air is drawn at flow rates up to 185 liters/minute through either or both of two parallel 15 cm composite filter pads comprised of Porapak® sandwiched between two layers of glass fiber mat.

The major advantage of the ERCO sampler for source air monitoring is that it provides a relatively large sample size with short sampling times. It is compact and light weight, which makes it highly portable. The model studied was equipped for either AC or DC power and could be operated on a heavy duty automobile battery at flow rates up to 160 liters/minute. The greatest disadvantage of the system is the high cost of the composite filter pads, which cannot be reused.

2. Low Volume Indoor Source Samplers

a. Pumps:

DuPont Constant Flow Sampling Pump, Model P4000A (includes charger), Catalog No. 66-241 (Fig. 8). DuPont, Applied Technology Division, Wilmington, DE 19898.

or

Figure 7. A high-volume air sampler developed for the U.S. Army by Environmental Research Corporation (ERCO). Shown to the right are the composite filter pads used to trap airborne pesticides.

MSA Monitaire™ Sampler, Model S, Catalog No. 458475 and charger No. 456059. Mine Safety Appliances Company, 600 Penn Center Boulevard, Pittsburgh, PA 15235.

Both of these small, battery operated pumps are capable of pumping air through an 18 mm diameter x 50 mm cylindrical PUF plug at 2.5 to 4 liters/minute for at least 8 hours with a fully charged battery pack. The DuPont pump (Fig. 8) has the advantage that it will automatically adjust its pumping rate to compensate for changes in flow resistance (e.g., due to accumulation of particulate matter at the intake of the collection module). It also operates more quietly than the MSA and can be programmed to stop sampling after a prescribed period.

b. Collection Devices:

Any glass, metal or Teflon cartridge capable of holding a cylindrical plug of polyurethane foam (approximate volume 15 to 20 cm^3) or 5 to 10 cm^3 of granular sorbent can be used. Several collection modules are shown in Figure 9, along with a portable pump.

Figure 8. The DuPont constant flow sampling pump (cover removed) and battery charger.

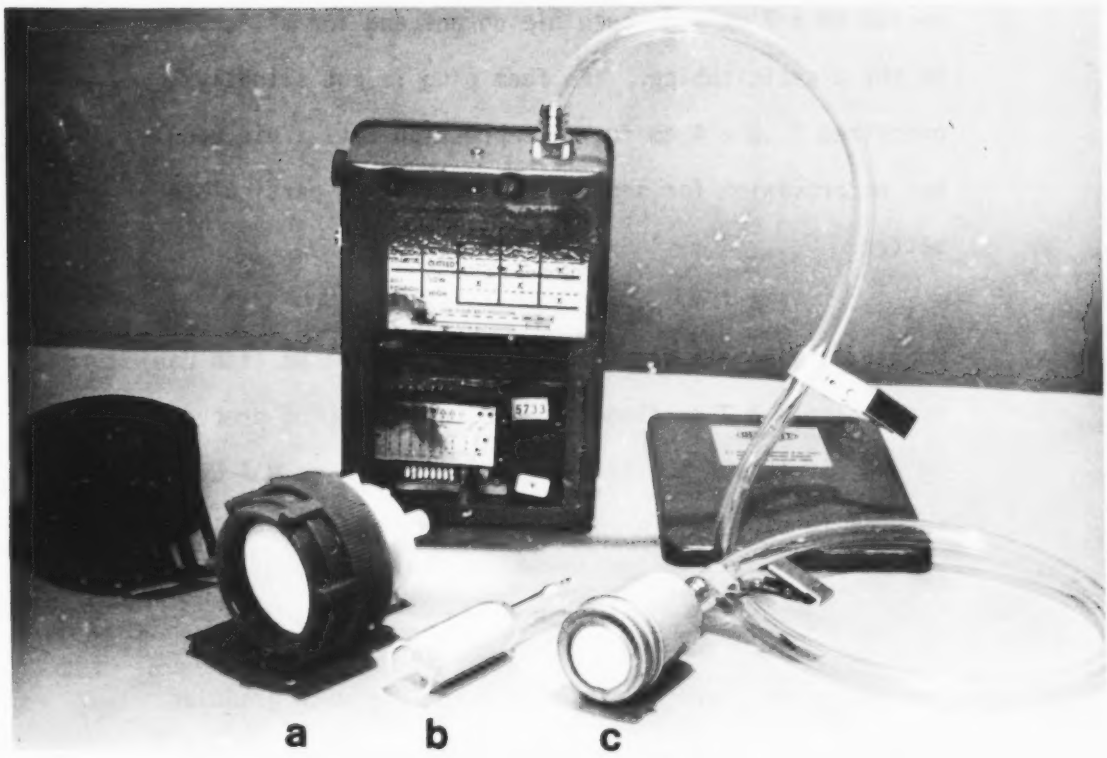

Figure 9. Personal sampling pump and three collection modules. (a) Polyurethane foam with particulate filter in an all Teflon container (b) polyurethane foam in glass holder, and (c) polyurethane foam with particulate filter in an all aluminium container.

Module a is an all Teflon container containing a 4.5 cm diameter x 3 cm foam plug preceded by a 5 cm diameter glass fiber filter (Gelman Type A or MSA CT-75428) mounted in the cap. This collection module should only be used for stationary sampling since it is too heavy to be worn.

Module b is an open glass tube, 2 cm i.d. x 5 cm, connected to a 7 mm o.d. open tip on one end for attachment to the plastic tubing. The foam plug is cut slightly oversized 2 cm x 4 cm for a compression fit. This module has no provision for separate collection of particulate matter.

Module c is an all aluminium container (a 35 mm film can) containing a 3.2 cm diameter x 3.5 cm foam plug preceded by a 3 cm glass fiber filter (Gelman Type A or MSA CT-75428) mounted in the cap. A Swageluk® hose nipple is sealed in the bottom of the can.

Modules b and c are most suitable for use with granular sorbents. It is suggested that small cylinders of polyurethane foam be inserted before and after the granular sorbent to retain the latter in place.

c. Preparation and Analysis of Sorbents and Glass Fiber Filters

Follow the same basic procedures described in section II,5. Scale down volumes for the smaller plugs or quantities of granular sorbents used. Smaller Soxhlet extractors will cycle more frequently (e.g., 8 cycles/hour). Because efficient extraction of pesticide from glass module b (Fig. 9) will probably not be achieved with the sorbent in place, extract the foam and sorbent separately. Cut glass fiber filters to size, wrap loosely in aluminum foil, heat to 315°C in a muffle furnace overnight to remove any organic material, and place in a desiccator until use.

d. Calibration of Air Sampler

For low volume samplers, a simple soap bubble meter is adequate for calibration. MSA pumps may also be calibrated by displacing water from an inverted graduated cylinder (1 or 2 L size) during a measured length of time.

Commercial calibration units are also available from Mine Safety Appliances (Catalog No. 457629), shown in Figure 10 and from DuPont (Catalog No. 66-242-f-1) as seen in Figure 11.

When polyurethane foam alone is used, as in module b (Fig. 9), the sampling pump may be calibrated without the module attached. However, the additional use of a prefilter or granular sorbents causes sufficient pressure drops across the sampling module to require calibration with the loaded module in place. In all cases, it is suggested that the loaded sampling module be installed during calibration, or there may be very large differences between the pump flow meter reading and actual flow through the module.

For calibration, some means of adapting the intake face of the module into the calibration system must be devised. For module b, laboratory "bubble" tubing (3/4 to 3/8 inch) may be used. (A suggested source of the latter is Sherwood Medical Industries, Argyle, NY). When a commerical calibration system is used, the manufacturer's instructions should be followed.

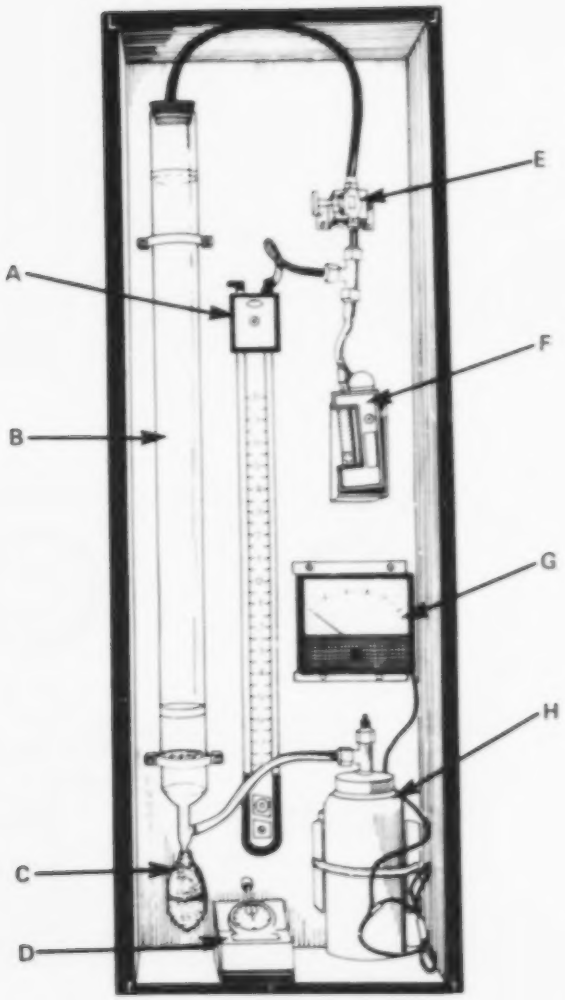

Figure 10. Calibration unit for the MSA personal sampling pumps. (a) Manometer, (b) soap bubble meter, one liter, (c) rubber bulb, (d) stop watch, (e) needle valve, (f) pump being calibrated, (g) voltmeter, 0-10 V, and (h) soap solution reservoir.

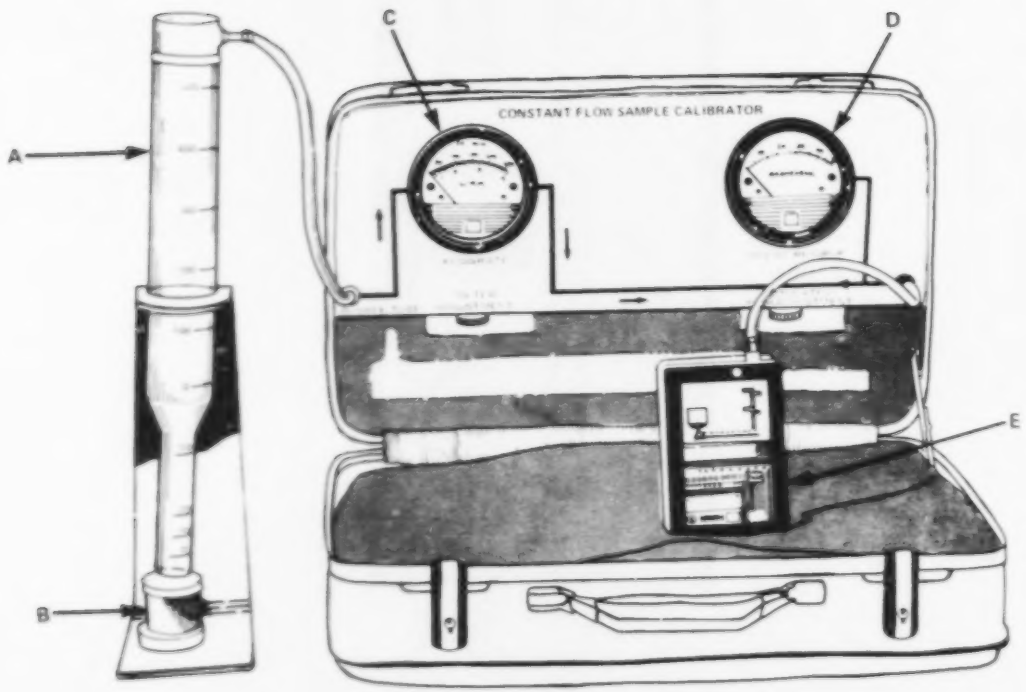

Figure 11. Calibration unit for DuPont personal sampling pumps: (a) Soap bubble meter, 500 ml; (b) soap solution reservoir; (c) flow rate meter; (d) pressure drop meter; (e) pump being calibrated.

e. Determination of Sampling Efficiencies for Specific Pesticides

Measured quantities of pesticides in a volatile solvent such as n-hexane are placed in a suitable container, such as a U-tube or a midget impinger, which is attached to the sampling module. The container should be temperature controlled with a heated water bath or heating block to slowly volatilize the pesticide. After the sampling period (which should be as long as that anticipated in actual monitoring studies), the amount of pesticide remaining in the container and that collected by the sorbent is determined to establish collection efficiency. Sampling periods should be 4 to 8 hours.

A unit can be constructed to facilitate the measurement of collection efficiencies. A midget impinger (Ace Glass Cat. No. 7531-10) with the nozzle cut off at the base of the joint and modified with an o-ring seal joint (Ace Glass Cat. No. 7664-110) at the side arm can be used to hold the pesticide solution. Two glass modules of the same type as sampling module b (2,b.) are constructed with O-ring seal joints (Ace Cat. No. 7664-116) on their large end. One of the modules also has an o-ring seal joint (Ace Glass Cat. No. 7664-110) on its small end.

With this system set up as shown in Figure 12, there are only glass connections between the pesticide solution and the sorbent. This avoids the use of plastics which results in a loss of efficiency.

f. Collection of Air Samples

For determination of pesticide residues indoors, air samples should be taken in as many locations as necessary to achieve a profile of the distribution throughout the building. In houses with forced-air heating and/or air conditioning, air concentrations will tend to be equilibrated, although there will probably be areas in rooms where circulation is impaired. Unlike the situation in outdoor air, there should be little diurnal variation in pesticide levels. Concentrations may vary more widely in houses without air circulating devices, and may also be weather dependent (i.e., depend on whether windows and doors to the outside are open or closed).

Nearly all domiciles and many other buildings are given preconstruction termite treatment. This results in a slow release of the insecticide over very long periods of time (at least up to 25 years). In buildings where circulation is poor, airborne termitacide levels may be

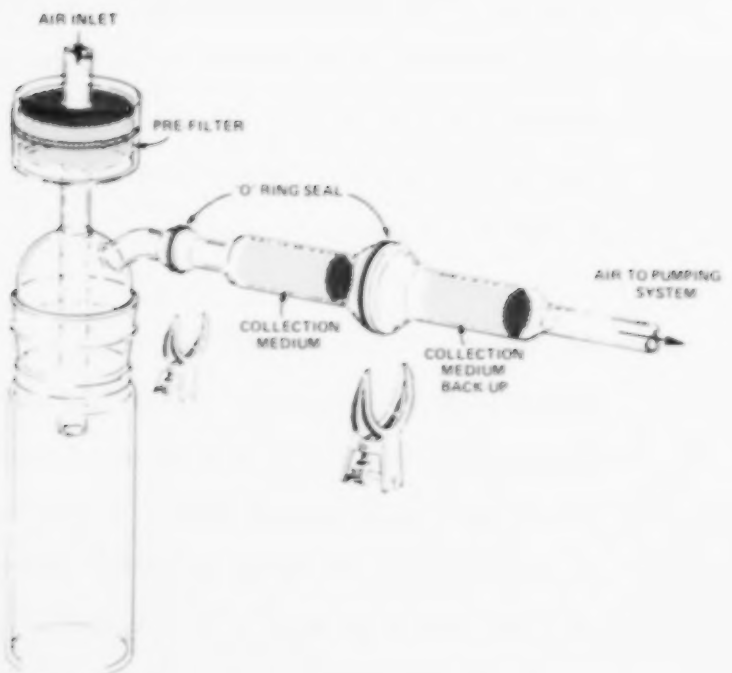

Figure 12. Midget impinger used for collection efficiency studies.

higher in basements or ground floors than on other floors. In plenum houses, the crawl space under the house serves as the plenum in the air distribution system, which contributes substantially to the transport of termitacide to other portions of the dwelling.

Kitchens and bathrooms are favorite areas for insects such as roaches, ants, and silverfish; consequently, the application of insecticides in these areas is common practice. The chemicals are usually applied in baits or in slow-release formulations, so that pesticides may be emitted into the air for many months after treatment. Similarly, crack and crevice treatment for pest control is popular in commercial buildings.

The design of the structure and history of its past control treatment should be taken into account when planning an air monitoring project. Several samplers should be used at once to obtain a distribution profile of pesticide levels in the building. Normally, an 8 hour sampling period at about 2 liters/minute is sufficient to obtain an adequate sample for analysis. In this period, about one m^3 of air is sampled, which should provide a detection limit of 0.1 $\mu g/m^3$ or lower for most pesticides. This level is one-tenth that of the National Institute of

Occupational Safety and Health proposed standard of 1 $\mu g/m^3$ for a 10 hour work day, 40 hour work week exposure to carcinogenic compounds. Although the portable pumps described earlier in this section are designed to operate for 8 hours on fully charged battery packs, house current (through the battery charger) should be used when available to assure more uniform pumping rates during the sampling period.

The air intakes of the sampling modules should be placed one or two meters above floor level and oriented downward or horizontally. If oriented upward, non-respirable pesticide loaded dust may be collected. If pesticide residues on household dust particles appear to be very significant, a prefilter should always be used.

IV. WORKPLACE AIR - PERSONNEL MONITORING:

Inhalation of airborne dust and vapors containing high concentrations of pesticides constitutes a serious hazard to pest control operators, pesticide formulators, and other persons occupationally involved in agricultural industry. Respiratory exposure can be best assessed through the use of a personal monitor worn on the body while working in areas of high pesticidal contamination.

1. Air Sampling Devices

The small sampling units described in the previous section are designed for personal monitoring. They are battery operated and can be worn on the body.

The MSA pump weighs 870 grams and may be worn comfortably on the waist belt. The DuPont pump is also designed to be attached to a waist belt, but is somewhat heavier (1.2 kg with battery packs that are required for 8 hours of operation). The ability of the DuPont pump to compensate for changes in flow resistance and to be programmed to stop sampling after a prescribed period more than make up for the slight inconvenience of its added weight. DuPont markets a smaller constant flow unit that weighs only 400 grams, but it draws only 200 ml/minute at full flow (no resistance). In order to achieve the sensitivity in the 0.1 to 1 $\mu g/m^3$ range for many pesticides, flow rates of 1 to 3 liters/minute are needed, particularly for sampling periods that are necessarily shorter than 8 hours. The sampling modules are attached to the shirt collar or lapel to monitor air in the breathing zone. The intake should be oriented downward to exclude large dust particles, which may not enter the nostrils.

It has been pointed out that estimation of respiratory exposure in areas of high pesticide concentration is accurate only for

true gases, due to the probable lack of uniform dispersion of particulate matter in the breathing zone. The aerodynamics of respiration through the nostrils is difficult to duplicate with an air sampler. Most sampling devices also will not differentiate between particles that would be trapped in the nasopharynx and the smaller respirable particles that reach the lungs. However, a small cyclone sampler that separates and discards nonrespirable particulates (above 10 μm in diameter) is marketed by Mine Safety Appliances. The unit, called the Gravimetric Dust Sampling Kit (MSA 456241), can be attached to the collar or lapel and is designed to sample at three calibrated flow rates (2.0, 1.8, and 1.6 liters/minute). Respirable particulate matter collected in a filter cassette may be analyzed for pesticide content. A separate vapor trap (and pump) could be worn for comparative data.

2. Preparation and Handling of Samples

Pre- and post-treatment of sampling devices and analytical procedures should be identical to those described in the preceding sections. Special care should be exercised to avoid contamination of samples in the field. Improper handling of the collection module before or after the sampling period could easily deposit a microgram of the material being monitored (or interfering substance) on the sampling medium, which would result in a false positive analysis of 1 $\mu g/m^3$. Therefore,

the collection modules should be loaded in the laboratory and sealed in hexane-rinsed aluminum foil or a clean, sealed glass jar before transport to the field. An analyst should carefully install the sampling device and instruct the wearer not to touch or disturb it. The analyst should be present at the end of the sampling period to remove the module, place it in a sealed container, and transport it back to the laboratory.

3. Sampling Duration

Sampling times should be commensurate with known or anticipated exposure times. If potential exposure to airborne pesticides is intermittent or brief, sampling should be performed only during those periods. If exposure is continuously uniform throughout the work day, sampling may be conducted for only a portion of the day and the result extrapolated to estimate the total exposure for the entire work period. If exposure is not uniform but occurs for regular periodic cycles during the work day, sampling should be conducted over the entire work day to obtain an accumulated total exposure assessment. The monitoring program selected should, of course, be the result of careful planning in order to provide a realistic assessment of worker exposure.

4. Estimation of Inspired Quantities

Since the sampling rates achievable with small, battery operated pumps are substantially lower than the respiratory rates of most workers, monitoring data must be extrapolated on the basis of estimated lung ventilation values to obtain an assessment of total exposure. Table 1 gives the average respiratory rates and their normal ranges for men and women at rest and at work.[10] Values would be lower for children and elderly people. Ideally, pulmonary function test (PFT) measurements should be made on the worker while performing the job in order to determine the exact respiratory rate. Since PFT equipment and personnel trained in its operation are not likely to be available, a subjective estimation must be made of the breathing rate if an approximation of the total quantity of pesticide inspired is desired. To the untrained eye, it may sometimes be difficult to differentiate between light and heavy work. Estimates of average respiration rates likely to be encountered among persons occupationally exposed to pesticides have been made by H. R. Wolfe based on many visual observations over many years. These estimates, which are given in Table 2, are subjective but may be better than inexperienced judgments. They should not be used a priori unless the data are appropriately qualified. Also, unless the sampler used can differentiate between respirable and nonrespirable particulate

Table 1

Normal Respiratory Rates for Humans*

Level of Activity	Respiratory Rates in Liters per Minute			
	Adult Male		Adult Female	
	Avg.	Range	Avg.	Range
Rest	7	6-10	4	4-7
Light Work	29	27-31	16	16-17
Heavy Work	60	50-90	24	17-32

*Data from reference 10.

Table 2

Subjective Estimations of Respiratory Rates for Pesticide Workers

Work Situation	Estimated Respiratory Rate (L/Min)	
Agricultural Workers:	Adult Male*	Adult Female**
Sprayer Using Hand Gun and Dragging Hose	50-67	22-25
Driver of Tractor Pulling Spray Equipment	18	10
Fruit Thinner or Picker	29-30	16
Flagger for Aircraft Spray Application	18	10
Pesticide Formulation Plant Workers:		
Bagger (Filling small bags - 2 to 5 lb.)	29-30	16
Bagger (Filling large bags - 50 lb.)	32-33	17
Stacker (Stacks 50 lb. bags or pallets)	33-42	17-20
Bagger and Stacker (Filling and stacking 50 lb. bags or pallets)	33-42	17-20
Boxer (Packing small bags into shipping boxes)	30-32	16-17
Fork Lift Operator	20	12
Mixer (emptying bags of dry pesticide into hopper for blending)	33	17
Worker cleaning inside of hoppers and bins	33	17

*Based on numerous visual observations of I. F. Wolfe[11] and the respiratory rates given in Table 1.

**Calculated as the percent of the male rate using data in Table 1.

matter, it cannot be assumed that the quantity of pesticides collected is proportional to the total inspired into the lungs.

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